Spontaneously Passivating Amorphous Fe-Cr-Mo-Metalloid Alloys in 6 N HCl at Room Temperature and 80°C

Spontaneously Passivating Amorphous Fe-Cr-Mo-Metalloid Alloys in 6 N HCl at Room Temperature and 80°C*

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Synopsis

Amorphous iron-base alloys capable of passivating spontaneously in 6 N HCl at 80°C were prepared by rapid quenching of molten alloys. The corrosion resistance and passivating ability of the alloys increased with increasing chromium and molybdenum contents. The critical concentrations of chromium and molybdenum in the alloys necessary for spontaneous passivation in 6 N HCl at room temperature and 80°C were established. These concentrations were greatly affected by coexisting metalloids. The passivating ability decreased in the order of alloys containing phosphorus, carbon, silicon and boron.

I. Introduction

Some amorphous chromium-bearing alloys prepared by rapid quenching from the molten state possess extremely high corrosion resistance[1)-7)]. In particular, they passivate spontaneously even in acidic chloride solutions and are immune to pitting and crevice corrosion even when they are polarized anodically. As well known, any crystalline stainless steel or nickel-base alloy cannot passivate spontaneously in 1 N HCl and almost all of them suffer pitting corrosion by anodic polarization in 1 N HCl. In contrast, the amorphous Fe-Cr-13P-7C alloys containing 8 atomic percent or more chromium passivate spontaneously in 1 N HCl at ambient temperature, and their passivity is stable up to the transpassive region of chromium[1)]. Such high corrosion resistance of the amorphous alloys are attributable to their chemical homogeneity and high reactivity. The former characteristic is responsible for the formation of

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a uniform passive film with a low activity of weak points in the film, and the latter leads to the rapid formation of a passive film in which beneficial species in providing the film with the high protective quality and high stablity are highly concentrated[7]-[9].

Hot concentrated hydrochloric acids are representative of the most aggressive environments and at present only tantalum has been industrially employed as a structural material in these environments. The corrosion-resistant ferrous alloys against these environments can be developed with the amorphous alloys which are able to possess an extremely high corrosion resistance. The most effective alloying addition in improving the corrosion resistance in acidic solutions is chromium. According to our XPS studies[5],[7]-[15], passive films formed on amorphous and crystalline chromium-bearing alloys are composed mainly of hydrated chromium oxyhydroxide, and hence its enrichment in the passive film is one of decisive factors in providing a high protective quality of the film. The amorphous alloys are able to concentrate remarkably chromic ions in the passive film[16]. Besides chromium, it is well known that addition of molybdenum also improves the corrosion resistance of amorphous chromium-bearing alloys[17],[18]. Our recent study[19] actually revealed that amorphous Fe-Cr-Mo-20B alloys containing sufficient amounts of chromium and molybdenum passivate spontaneously even in 6 N HCl at ambient temperature.

The work reported herein aims to prepare amorphous alloys having the high corrosion resistance in hot concentrated hydrochloric acids and to determine borders in alloying concentrations of chromium and molybdenum necessary for spontaneous passivation of amorphous Fe-Cr-Mo-metalloid alloys in 6 N HCl at different temperatures.

II. Experimental

Sixty alloys were first cast into rod-shaped ingots by water-quenching of alloy melts, after the alloy melts were prepared by induction melting of commercial metals and ferro-alloys under an argon atmosphere and then they were sucked up into quartz tubes. Rapid quenching to obtain the amorphous structure was performed by the rotating wheel method after remelting the alloy ingot in a quartz tube under an argon atmosphere. The formation of the amorphous structure of the alloys was confirmed by X-ray diffraction.

Average corrosion rates of the alloys were estimated from weight losses during immersion tests. The specimen weights were measured by a microbalence before and after immersion tests. After immersion specimens were rinsed with deionized water and methyl alcohol, but specific

procedures to remove corrosion products from the specimens were not applied. Anodic polarization curves of the alloys were measured potentiodynamically from the corrosion potential with a potential sweep rate of 2.38×10^{-3} V·s^{-1}. Prior to the measurements of corrosion rates and polarization curves, the alloys were polished mechanically in cyclohexane with silicon carbide paper to No. 1500 to remove an oxide layer formed during preparation of the amorphous alloys. The solution used was 6 N HCl which was prepared by using reagent grade chemical and deionized water. The solution temperature during the measurements at room temperature was about 25 ± 2°C. The measurements in hot hydrochloric acid were carried out at 80 ± 1°C, that was the highest temperature where disconnection of the circuit inside a Luggin capillary due to bubble formation in this concentrated hydrochloric acid was avoidable.

III. Results

Potentiodynamic anodic polarization curves of various amorphous Fe-Cr-Mo-13P-7C alloys measured at room temperature are shown in Figures 1-3. Increasing content of either chromium or molybdenum decreases the current densities in both the active and passive regions. When the molybdenum content is raised up to 10 atomic percent, the amorphous Fe-Cr-Mo-13P-7C alloys containing 5 atomic percent or more chromium pas-

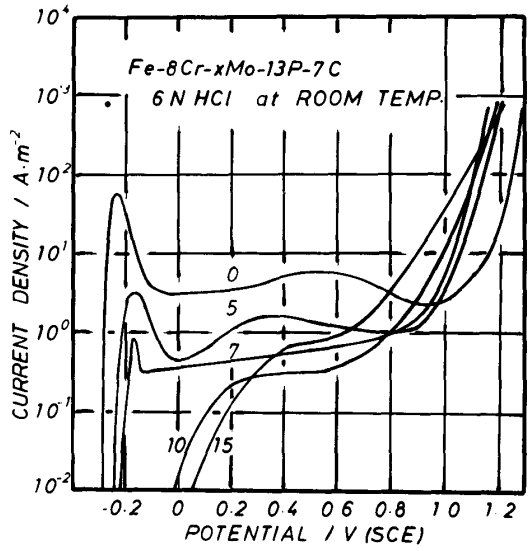

Figure 1. Potentiodynamic anodic polarization curves of amorphous Fe-8Cr-xMo-13P-7C alloys measured in 6 N HCl at room temperature. The number attached to a respective curve in the figure denotes the molybdenum content in atomic percent.

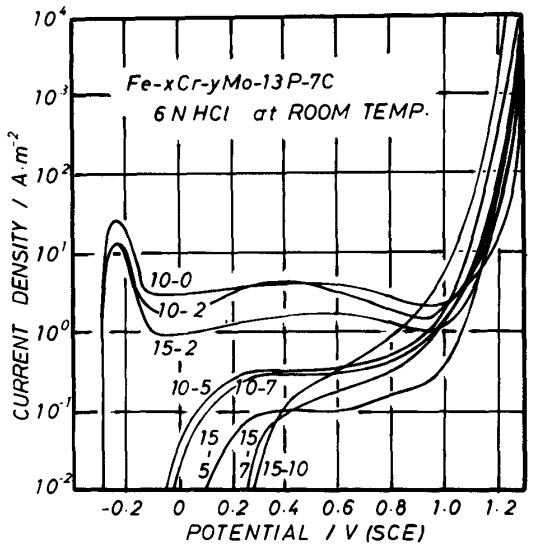

Figure 2. Potentiodynamic anodic polarization curves of amorphous Fe-xCr-yMo-13P-7C alloys measured in 6 N HCl at room temperature. The first and second numbers attached to a respective curve denote chromium and molybdenum contents, respectively, in atomic percent.

sivate spontaneously in 6 N HCl at room temperature. When these alloys contain 10 atomic percent or more chromium, addition of 5 atomic percent molybdenum is sufficient to lead to spontaneous passivation. When the chromium content is still high, the molybdenum addition necessary for spontaneous passivation is further decreased; Fe-20Cr-2Mo-13P-7C alloy and Fe-25Cr-13P-7C alloy without molybdenum addition passivate spontaneously. It is interesting that the addition of a large amount of molybdenum such as 15 atomic percent to Fe-8Cr-13P-7C alloy or 10 atomic percent to Fe-10-15Cr-13P-7C alloys raises the corrosion potential indicating the beneficial effect of molybdenum for passivation, but also raises the current density at high potential in the passive region suggesting detrimental effect of molybdenum at high potentials.

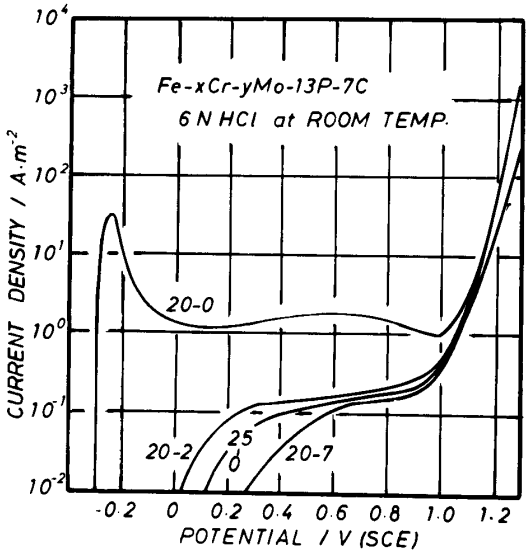

Figure 3. Potentiodynamic anodic polarization curves of amorphous Fe-xCr-yMo-13P-7C alloys measured in 6 N HCl at room temperature. The first and second numbers attached to a respective curve denote chromium and molybdenum contents, respectively, in atomic percent.

Figures 4 and 5 show anodic polarization curves of amorphous Fe-

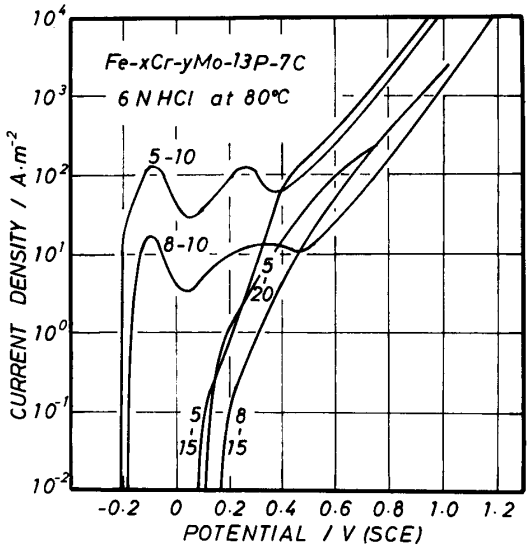

Figure 4. Potentiodynamic anodic polarization curves of amorphous Fe-xCr-yMo-13P-7C alloys measured in 6 N HCl at 80°C. The first and second numbers attached to a respective curve denote chromium and molybdenum contents, respectively, in atomic percent.

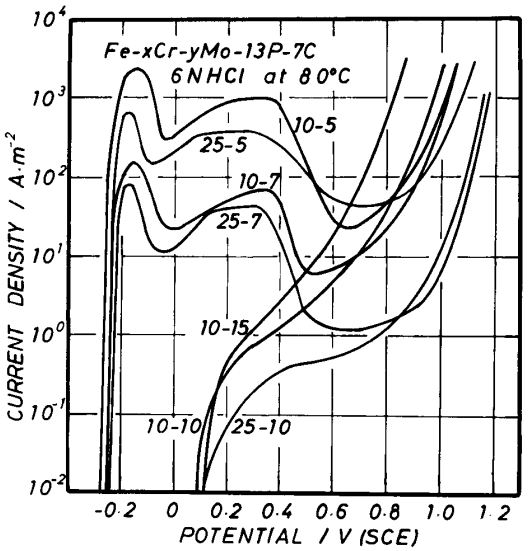

Figure 5. Potentiodynamic anodic polarization curves of amorphous Fe-xCr-yMo-13P-7C alloys measured in 6 N HCl at 80°C. The first and second numbers attached to a respective curve denote chromium and molybdenum contents, respectively, in atomic percent.

Cr-Mo-13P-7C alloys measured in 6 N HCl at 80°C. Similarly to the results obtained at room temperature, increasing contents of both chromium and molybdenum decrease the anodic current density in the active and passive regions. However, because the solution became further aggressive by rise in the temperature, the current density in the active and passive regions is significantly higher than that measured at room temperature. When the molybdenum concentration is raised to 15 atomic percent, the amorphous Fe-5-8Cr-Mo-13P-7C alloys passivate spontaneously in 6 N HCl at 80°C. A small rise in polarization potential from the corrosion potential results in a sharp increase in the anodic current density of spontaneously passivating alloys containing relatively low chromium due to a severe attack by this aggressive solution as can be seen in Figure 4. A comparison between Figures 3 and 5 clearly reveals that a rise in solution temperature from room temperature to 80°C requires the addition of higher amounts of chromium and/or molybdenum for spontaneous passivation; the addition of 10 atomic percent molybdenum is necessary for spontaneous passivation of amorphous Fe-25Cr-13P-7C alloy at 80°C.

When the chromium content exceeds 25 atomic percent, preparation of amorphous Fe-Cr-Mo-18C alloys is much easier to that of amorphous Fe-Cr-Mo-13P-7C alloys. Accordingly, the corrosion resistance of amorphous high chromium alloys was examined by using the amorphous Fe-Cr-Mo-18C alloys. Figure 6 shows anodic polarization curves of amorphous

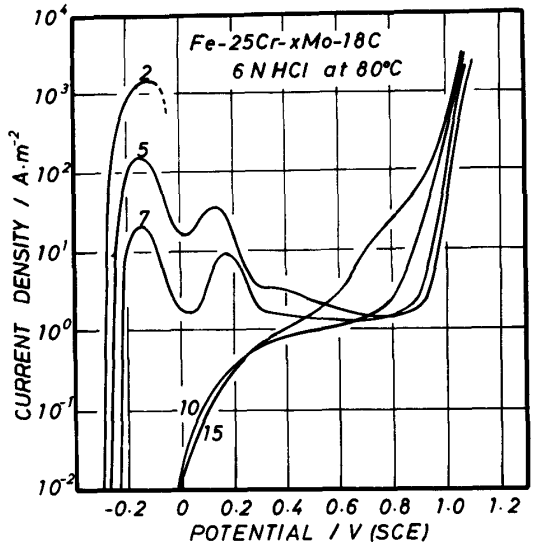

Figure 6. Potentiodynamic anodic polarization curves of amorphous Fe-25Cr-xMo-18C alloys measured in 6 N HCl at 80°C. The number attached to a respective curve denotes the molybdenum content in atomic percent.

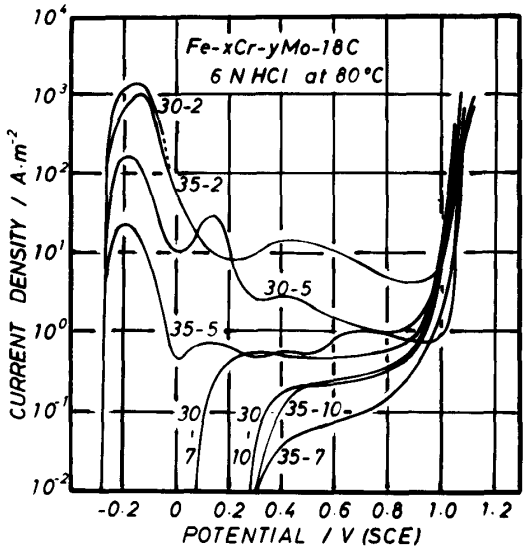

Figure 7. Potentiodynamic anodic polarization curves of amorphous Fe-xCr-yMo-18C alloys measured in 6 N HCl at 80°C. The first and second numbers attached to a respective curve denote chromium and molybdenum content in atomic percent.

Fe-Cr-Mo-18C alloys. When 10 atomic percent or more molybdenum is added, the amorphous Fe-25Cr-Mo-18C alloys passivate spontaneously, similarly to the amorphous Fe-25Cr-Mo-13P-7C alloys. However, as can be seen from a comparison between Figures 5 and 6, even when spontaneous passivation occurs, the amorphous Fe-25Cr-Mo-18C alloys show lower corrosion potentials and higher anodic current densities in comparison with the amorphous Fe-25Cr-Mo-13P-7C alloys containing the same amount of molybdenum, suggesting that the corrosion resistance of the 18C alloys is lower than the 13P-7C alloys. As shown in Figure 7, at still higher chromium contents, the molybdenum concentration necessary for spontaneous passivation in the hot concentrated hydrochloric acid can be decreased.

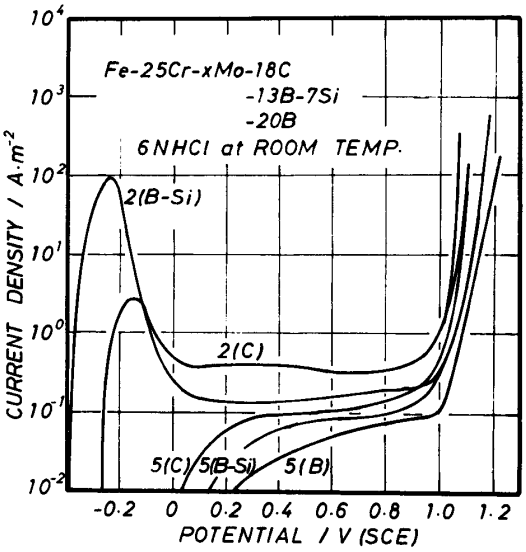

Figure 8. Potentiodynamic anodic polarization curves of amorphous Fe-25Cr-xMo-metalloid alloys measured in 6 N HCl at room temperature. The number attached to a respective curve denotes the molybdenum content in atomic percent. Symbols of elements, such as C, B-Si and B correspond to 18C, 13B-7Si and 20B, which are contained in the amorphous alloys.

Figures 8 and 9 show effects of metalloid additions on anodic polarization curves. The amorphous Fe-25Cr-2Mo alloys containing 18C, 13B-7Si or 20B cannot passivate spontaneously in 6 N HCl at room temperature, despite the fact that the amorphous Fe-25Cr-13P-7C alloy without molybdenum addition passivates spontaneously in this solution as shown in Figure 3. When the solution temperature is raised to 80°C, spontaneous passivation takes place only on the 18C and 13P-7C alloys among the amorphous Fe-25Cr-10Mo-metalloid alloys, although the 18C alloy shows the higher anodic current density and lower corrosion potential than the 13P-7C alloy, indicating that the corrosion resistance of the 13P-7C alloy is higher than that of the 18C alloy. The amorphous Fe-25Cr-Mo-13B-7Si alloys can passivate spontaneously

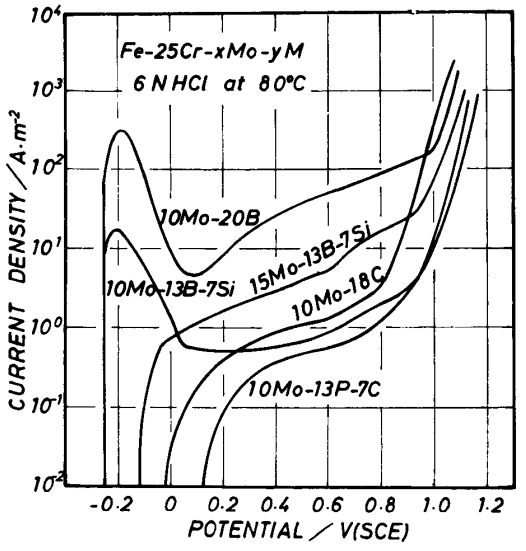

Figure 9. Potentiodynamic anodic polarization curves of amorphous Fe-25Cr-xMo-metalloid alloys measured in 6 N HCl at 80°C.

when the molybdenum concentration is 15 atomic percent or more. However, the corrosion resistance of the amorphous Fe-25Cr-15Mo-13B-7Si alloy is lower than that of the amorphous Fe-25Cr-10Mo-18C alloy, since the former exhibits lower corrosion potential and higher anodic current density than the latter alloy.

In order to confirm the fact that spontaneous passivation sharply decreases the corrosion rate, average corrosion rates of amorphous Fe-Cr-Mo-13P-7C alloys containing 10 and 25 atomic percent chromium were estimated from the weight loss during the immersion test. The corrosion rates are shown as a function of molybdenum content in Figure 10. Corrosion rates of crystalline type 304 stainless steel, pure titanium and pure tantalum measured in 6 N HCl at 80°C are also shown for comparison. When molybdenum addition is not sufficient, a thick corrosion product was formed on the specimen surfaces particularly at 80°C, and it could not be removed by rinsing with water. Since the corrosion rate was estimated from the weight loss during the immersion test, the corrosion rate of the specimen covered by the thick corrosion product is greatly underestimated, and hence arrows in the figure indicate that the true corrosion rate is significantly higher than that written in the figure. For instance, the corrosion rate of amorphous Fe-10Cr-13P-7C or Fe-10Cr-2Mo-13P-7C alloy measured at room temperature is apparently higher than those estimated from the weight loss after immersion test at 80°C, because the specimen surfaces immersed at 80°C were covered by a thick corrosion product, and hence the true corrosion rate must be considerably higher than that measured at room temperature. Comparison of this figure with Figure 2 clearly reveals that spontaneous passivation in 6 N HCl at room temperature due to the addition of 5 atomic percent or more molybdenum to the amorphous Fe-10Cr-13P-7C alloy leads to about five orders of magnitude decrease in the corrosion rate. An increase in the solu-

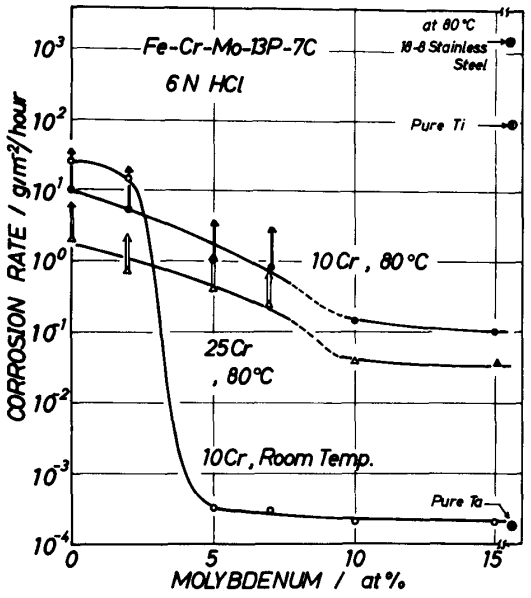

Figure 10. Change in corrosion rates of amorphous Fe-10Cr-xMo-13P-7C and Fe-25Cr-xMo-13P-7C alloys in 6 N HCl at room temperature and 80°C as a function of molybdenum content. The corrosion rate was estimated from the weight loss during the immersion test. A thick corrosion product was formed on the low molybdenum alloys and it could not be removed by rinsing with water. Accordingly, arrows indicate that the true corrosion rate would be significantly higher than that written in the figure.

tion temperature leads to about three orders of magnitude increase in the corrosion rate in the passive state, but even at 80°C, passivation is still quite effective in decreasing the corrosion rate. It is interesting that the addition of a sufficient amount of molybdenum gives rise to a sharp decrease in the corrosion rate based on spontaneous passivation, but further addition of molybdenum to the spontaneously passivating alloys is not effective in decreasing the corrosion rate. In contrast, an increase in the chromium content of the spontaneously passivating alloys significantly decreases the corrosion rate. On the other hand, the corrosion rates of the spontaneously passivating amorphous alloys are several orders of magnitude lower than those of crystalline stainless steel and pure titanium. The corrosion resistance of the amorphous Fe-25Cr-15Mo-13P-7C alloy in 6 N HCl at 80°C, however, is not as high as that of pure tantalum. Accordingly, for the purpose to develop amorphous ferrous alloys whose corrosion resistance is comparable to tantalum in hot concentrated hydrochloric acids, other factors than spontaneous passivation must be taken into account.

Since spontaneous passivation greatly decreases the corrosion rate the effect of chromium and molybdenum concentrations on the active-passive transition of amorphous Fe-Cr-Mo-metalloid alloys are summarized in Figure 11. Increasing contents of both chromium and molybdenum are effective for spontaneous passivation. Sufficient addition of chromium leads to spontaneous passivation in 6 N HCl at room temperature even if molybdenum is not added, while, unless chromium is added, any large amount of molybdenum addition to amorphous Fe-13P-7C[20] and Fe-18C[17] alloys does not result in spontaneous passivation even in diluted hydrochloric acids.

IV. Discussion

It is most striking that amorphous iron-base alloys can passivate spontaneously even in 6 N HCl at 80°C. The fact that iron-base alloys show such high corrosion resistance is at-

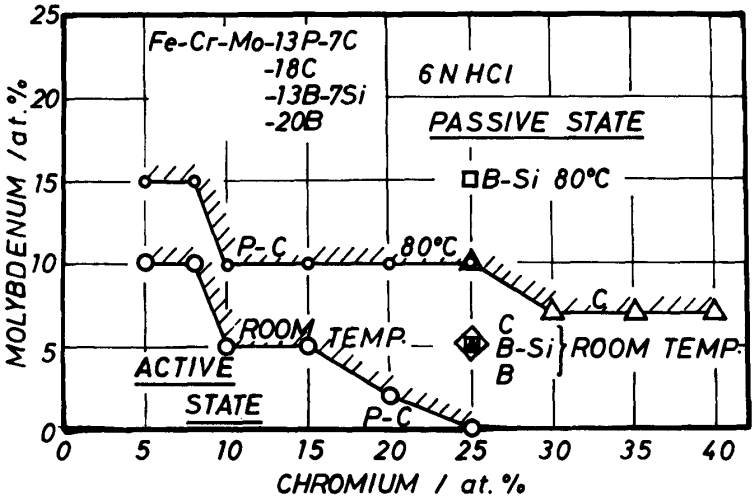

Figure 11. Critical concentrations of chromium and molybdenum for the active-passive transition of amorphous Fe-Cr-Mo-metalloid alloys in 6 N HCl at room temperature and 80°C.

tributable to the characteristics of amorphous metal-metalloid alloys.

Spontaneous passivation owing to increasing chromium and molybdenum contents occurs similarly at room temperature and 80°C. Consequently, the passivating species or composition of the passive film formed at 80°C seems similar to that formed at room temperature. According to our XPS study[19], passivation of amorphous Fe-Cr-Mo-metalloid alloys in 6 N HCl at room temperature occurs by the formation of a passive film consisting mainly of hydrated chromium oxyhydroxide. On the other hand, molybdenum does not constitute the passive film but it assists the formation of the passive hydrated chromium oxyhydroxide film as follows[7][13][14][19][21][22]: Active dissolution of alloys, which is necessary to accumulate beneficial metallic ions and/or OH^- ions at the alloy-solution interface prior to the passive film formation in aggressive solutions, leads to the formation of a molybdenum-enriched corrosion product film which slows down the dissolution rate of passivating species through the film. This fact accelerates the formation of a passive hydrated chromium oxyhydroxide film between the corrosion product film and the underlying alloy. The corrosion product film is formed as a result of active dissolution and is not stable at high potentials in the passive region of iron-base alloys. Accordingly, when the condition for the rapid supply of molybdenum to form the corrosion product film fails by lowering of the dissolution rate through the passive film formation, the corrosion product film dissolves in the solution. Therefore, molybdenum is greatly effective for passivation. Nevertheless, the passive film does not contain an appreciable amount of molybdenum as mentioned above.

The roles of chromium and molybdenum in passivating the alloys in hot concentrated hydrochloric acids may be the same as those in cold hydrochloric acids. Accordingly, an increase in chromium. which is able to form its own passive film, is quite effective for the formation of the passive film on the amorphous alloys in hot concentrated hydrochloric acids. As shown in Figure 3, at room temperature, sufficient additions of chromium lead to spontaneous passivation in 6 N HCl even if molybdenum is not added. The addition of molybdenum, which assists the passive film formation, is also necessary for spontaneous passivation in aggressive hot concentrated hydrochloric acids. However, molybdenum does not constitute the passive film, and hence amorphous Fe-Mo-metalloid alloys without chromium cannot passivate spontaneously even in 1 N HCl at room temperature[17][20]. Furthermore, molybdenum is unstable in the passive potential region of iron-base alloys due to transpassive dissolution. Thus the addition of excess molybdenum does not effectively improve the corrosion resistance at the open circuit potential and is rather detrimental than beneficial owing to transpassive

dissolution of molybdenum when specimens are polarized at high potentials in the passive region of iron-base alloys[19]. Consequently, as can be seen in Figures 4 and 5, the amorphous Fe-5-10Cr-15Mo-13P-7C alloys show a sharp increase in the passive current density by slight anodic polarization due to transpsssive dissolution of excess molybdenum.

The role of chromium and molybdenum in the formation of a passive film must be the same in amorphous and crystalline alloys. However, any large amount of chromium and molybdenum additions to crystalline iron does not lead to spontaneous passivation even in 1 N HCl at room temperature. Consequently, spontaneous passivation of amorphous ferrous alloys in hot concentrated hydrochloric acids is attributable to the following characteristics of amorphous metal-metalloid alloys; the chemical homogeneity of the alloys and the rapid accumulation of chromic ions in a high concentration in the passive film.

According to our study of change in the corrosion resistance of amorphous alloys by heat treatment[23], compositional fluctuations such as precipitates, segregates and other composition gradients mainly act as active surface sites with respect to corrosion. The amorphous alloys are free of defects associated with the crystalline state. Furthermore, they are prepared by rapid quenching from the molten state, which prevents solid state diffusion to form various compositional fluctuations. Such a chemically homogeneous nature of amorphous alloys is partly responsible for the high corrosion resistance and high passivating ability of amorphous alloys in hot concentrated hydrochloric acids.

As mentioned previously, the higher the concentration of hydrated chromum oxyhydroxide in the passive film, the higher is the protective quality of the film. For the accumulation of beneficial species such as chromic ions in the surface film, other constituents of the alloys should dissolve into the solution. A slow dissolution will result in the formation of a corrosion product film whose composition will be proportional to that of the underlying bulk alloy. On the contrary, when the active dissolution rate is very high due to the high reactivity of the alloy, relatively stable solid species such as hydrated chromium oxyhydroxide will preferentially accumulate at the alloy-solution interface and a chromium-concentrated passive film will be rapidly formed. Amorphous metal-metalloid alloys have this characteristic. As can be seen from the fact that amorphous Fe-metalloid alloys without adding a second metallic element are rapidly corroded in comparison with crystalline iron[18], when a stable surface film is not formed the amorphous alloys are more reactive than crystalline metals corresponding to the major constituents of the amorphous alloys[24]. Because

of such a high reactivity of amorphous metal-metalloid alloys, the amorphous alloys containing passivating elements are able to rapidly form passive films in which beneficial species are highly concentrated[16]. This is partly responsible for such high corrosion resistance that even iron-base alloys can passivate spontaneously in aggressive hot concentrated hydrochloric acids.

Although the active dissolution rate of the amorphous metal-metalloid alloys is more rapid than the crystalline metals, the rate is significantly different with metalloids contained in the alloys. Figures 8 and 9 indicate that the passivating ability of amorphous alloys is greatly affected by metalloids contained in the alloys and decreases in the order of the alloys containing phosphorus, carbon, silicon and boron. The dissolution rate of amorphous alloys containing these metalloids increases in that order[7]. In addition, metalloids affect the composition of anions in the passive film[9]; boron and silicon contained in amorphous alloys tend to form borate and silicate in the surface film with a consequent decrease in enrichment of protective oxyhydroxide in the film. Although chromium-bearing amorphous metal-metalloid alloys are all suitable to accumulate hydrated chromium oxyhydroxide in the passive film, among metalloids contained in the alloys, phosphorus is most effective since it has the highest ability to concentrate chromic ions in the passive film which is almost free of phosphate. Carbon also is not contained in the passive film, and hence does not disturb the formation of the pure oxyhydroxide film with a high protective quality. However, it does not so greatly accelerate the accumulation of beneficial species in the surface film as phosphorus does. Accordingly, next to phosphorus, carbon is the most effective metalloid in improving the corrosion resistance of amorphous metal-metalloid alloys. On the other hand, boron and silicon do not greatly favor chromium enrichment in the film, and they do not enhance the formation of hydrated chromium oxyhydroxide in the film since they form chromium borate and chromium silicate in the film. These difference in the role of metalloids in improving the corrosion resistance of amorphous alloys can interpret the difference in the passivating ability of amorphous alloys appeared in Figures 8 and 9.

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